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THIANTHRENE CONTAINING POLYIMIDES with MONOMER FORMATION via NUCLEOPHILIC AROMATIC SUBSTITUTION

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ABSTRACT: Thianthrene-2,3,7,8-tetracarboxylic dianhydride was synthesized via nucleophilic aromatic substitution of N-phenyl-4,5-dichlorophthalimide with thiobenzamide, thioacetamide and sodium sulfide. This monomer was then polymerized with aromatic diamines by the conventional low temperature technique in *N,N*-dimethylacetamide (DMAc) to yield soluble poly(amic acid)s. Polyimides were obtained by thermal cyclization of the poly(amic acid) films. Polymers obtained formed creasable thin films and had excellent thermal stability in air and nitrogen. The bent thianthrene structure limited crystallization and chain-packing as indicated by X-ray analysis. The highly amorphous thianthrene containing polyimides were only soluble in H_2SO_4.

Introduction

Polyimides are an important class of commercial polymers possessing outstanding thermal behavior combined with excellent mechanical properties.[1] A large number of derivatives have been synthesized starting from a variety of aromatic or aliphatic diamines or diisocyanates in reaction with tetracarboxylic acids and dianhydrides.[2] Most successful syntheses involve ring-opening of a dianhydride by a diamine to give poly(amic acid)s that are soluble and capable of processing by solution methods. Imidization in solution usually gives insoluble and infusible

polyimides for those derivatives possessing the best combination of physical properties. This generally requires that solution-cast films, fibers and prepregs of poly(amic acid) be thermally cured to the desired polyimide in their end-use forms.

Thianthrene-containing monomers and polymers offer potential thermal stability and processability that may make available a new family of semi-rigid, high-performance polymers. Thianthrene-based polyimides and polyamides have been reported by others using thianthrene diamines with aryl dianhydrides and aryl or aliphatic diacid chlorides, respectively[3,4,5,6] These polymers had decreased thermal stability, but good solubility compared to similar polymers containing phenyl thioether units. Property differences were attributed to the reduction in crystallinity caused by the non-planar shape of the thianthrene units disrupting packing of the polymers. Good thermal stabilities were obtained, however, for thianthrene-containing polyketones. These polymers were also highly amorphous, but with tne thianthrene units functionalized with carbonyl groups rather than amide nitrogens. The thermal stability of thianthrene-based polymers may depend on basic chemical and electronic structures as well as on crystallinity, intermolecular interactions and polymer chain packing.

Derivatized thianthrene molecules are usually prepared by either functionalizing preformed thianthrene[3,7,8] or starting with the functionality present before hetercycle formation.[4,9,10] The latter was used to obtain thianthrene-2,3,7,8-tetracarboxylic acid from the reaction of 4-mercapto-5-bromophthalic acid with Cu_2O. Our research group used alternative starting materials, 4,5-dichlorophthalimide plus thiobenzamide or

sodium sulfide, which are more readily available and less expensive.[11] Here, the carbonyl functionality was protected while the thioether units were formed by nucleophilic aromatic substitution (NAS).

During the course of this project, an industrial colleague pointed out a recent patent also describing the key thianthrene monomer and its conversion to polyimides.[12] We were in the process of carrying out detailed intermediate, monomer and polymer characterization (described here) which extends this approach beyond the patent results. In addition, we employed thiobenzamide and thioacetamide as alternatives to sodium sulfide for forming thioether linkages in general, and thianthrenes specifically.

The results reported here focus on thioether and thianthrene bond formation via NAS of *N*-phenyl-4,5-dichlorophthalimide, the synthesis of thianthrene-2,3,7,8-dianhydride, and it's use in the formation of thianthrene containing polyimides.

Experimental

All chemicals were purchased from Aldrich Chemical Company. Aniline was purified by vacuum distillation from sodium hydroxide. Thiophenol was stirred over $CaCl_2$ for 24 h followed by vacuum distallation. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were purified by vacuum distillation from calcium hydride. Anhydrous sodium sulfide was prepared from the nonahydrate by storing under vacuum in the presence of P_2O_5 and gradually increasing the temperature to 105 °C. Thiobenzamide was recrystallized from methanol. 4,4'-Oxydianiline (ODA) and 1,4-phenylenediamine (p-PDA) were purified

by recrystallization from ethanol followed by sublimation. 4,4'-Methylenedianiline (MDA) and 1,3-phenylenediamine (m-PDA) were purified by vacuum distillation. Anhydrous potassium carbonate, acetic anhydride and 4,5-dichlorophthalic acid were used as received.

Characterization

Solution NMR spectra were obtained on a Bruker AC-300 using standard parameters and DMSO-d_6 or $CDCl_3$ as solvents and secondary standards. Solid-state NMR spectra were acquired on a Bruker MSL-200 spectrometer operating at a frequency 50.32 MHz for carbon. The cross-polarization/magic angle spinning technique (CP/MAS) was used along with high-power proton decoupling during data acquisition. The proton and carbon spin locking rf fields were 68 kHz, and the rate of sample rotation for all spectra was > 4.0 kHz. FTIR spectra were taken on a Perkin-Elmer 1600 spectrometer. Differerential scanning calorimetry (DSC) was conducted on a TA Instruments 2920 DSC module (2100 data station) at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were performed with a TA Instruments 2960 TGA module (2100 data station) at a heating rate of 10 °C/min in nitrogen and air atmospheres. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

4,5-Dichlorophthalic anhydride (1). 4,5-Dichlorophthalic acid (51.33 g, 218.4 mmol) was refluxed in 100 mL of acetic anhydride for 2 h. The reaction flask was cooled to 70 °C and equipped with a distallation arm and an addition funnel with 125 mL of mixed xylenes. Excess acetic anhydride and product acetic acid were removed

by distillation and replaced by xylenes at a rate sufficient to keep the volume constant. Upon cooling to ambient temperature, the product crystallized out of solution. The precipitate was filtered, washed with cold benzene, dissolved in CH_2Cl_2, extracted with cold $NaHCO_3$, rotory evaporated to remove the solvent, and vacuum dried; yd 36.05 g (76%); mp 189-191 °C (lit[13] mp 188-190 °C); ^1H NMR (DMSO-d_6): δ 8.46 (s); ^{13}C NMR (DMSO-d_6): δ 161.4, 139.2, 131.4, 127.2.

***N*-Phenyl-4,5-dichlorophthalimide (2).** 4,5-Dichlorophthalic anhydride (**1**, 21.71 g, 100.0 mmol) was dissolved in 160 mL glacial acetic acid and 120 mL of DMAc under nitrogen. After the homogeneous solution was chilled to 10 °C, a solution of aniline (9.34 g, 100 mmol) in 30 mL of DMAc was added dropwise over 25 min. The reaction flask was heated at 150 °C for 8 h. Upon cooling to ambient temperature, plate-like crystals formed and were collected by filtration, washed with water, dried under vacuum at 60 °C, and recrystallized from ethyl acetate; yd 21.98 g (75%); mp 214-216 °C (lit[13] mp 214-215 °C); IR (KBr pellet): 1724, 1714, 1711, 1400, 1376, 1144, 1126, 741, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.43-7.57 (m, 5H), 8.30 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 164.4, 137.3, 131.4, 131.0, 128.3, 127.6, 126.3, 124.9.

***N*-Phenyl-4,5-dithiophenoxyphthalimide (3).** Thiophenol (0.8209 g, 7.451 mmol), potassium hydroxide (0.4826 g, 7.406 mmol), 20 mL of DMAc and 10 mL of toluene were combined in a reaction vessel equipped with a distallation arm. The mixture was heated to azeotropically remove water of reaction and excess toluene. The reaction vessel was cooled to ambient temperature and *N*-phenyl-4,5-

dichlorophthalimide (**2**, 1.031 g, 3.530 mmol, 0.95 equivalents) was added turning the color deep brown. Within minutes the mixture turned yellow and became heterogeneous. The mixture was heated at 90 °C for 2.5 h and cooled. The product was isolated by precipitating into 1:1 CH_3OH / H_2O, filtering, washing with CH_3OH and vacuum drying at 60 °C; yd 1.55 g (90.2%); mp 239-241 °C; ^{13}C NMR (DMSO-d_6): δ 166.1, 143.6, 133.9, 131.7, 130.5, 130.2, 129.9, 129.4, 128.8, 128.1, 127.2, 121.9.

***N*-Phenyl-4-thiophenoxy-5-chlorophthalimide (4).** Thiophenol (0.4171 g, 3.786 mmol), potassium hydroxide (0.2446 g, 3.754 mmol), 20 mL of DMAc and 10 mL of toluene were combined in a flask equipped with a distallation arm. The mixture was heated to azeotropically remove the water of reaction and excess toluene. In another flask, *N*-phenyl-4,5-dichlorophthalimide (**2**, 1.104 g, 3.779 mmol) was dissolved in 35 mL of DMAc and 15 mL of toluene. The mixture was kept under a nitrogen atmosphere and cooled to 15 °C. The thiophenoxide mixture was added slowly to the latter mixture through an addition funnel. The reaction mixture was kept at ambient temperature for 8 h followed by distillation to remove toluene. The product was isolated by precipitation into 1:1 CH_3OH / H_2O, washed with CH_3OH and vacuum dried; yd 1.100 g (80 %).

***N,N'*-Diphenylthianthrene-2,3,7,8-tetracarboxylic bisimide (5).**

Method A: *N*-Phenyl-4,5-dichlorophthalimide (**2**, 14.61 g, 50.01 mmol), thiobenzamide (7.55 g, 55.0 mmol) and anhydrous potassium carbonate (7.60 g, 55.0 mmol) were reacted in 100 mL of DMAc at 150 °C for 12 h under nitrogen. (Use of thioacetamide gave essentially the same results). After cooling to ambient

temperature, the yellow heterogenous reaction mixture was poured into 700 mL of water. The precipitate was filtered, washed with water, washed with CH_3OH and vacuum dried at 65 °C; yd 11.2 g (90 %); mp 369-371 °C; FTIR (KBr pellet): 1776, 1719, 1600, 1500, 1371, 1311, 1219, 1112, 747 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.41-7.51 (m, 10 H), 8.05 (s, 4 H); ^{13}C NMR ($CDCl_3$): δ 165.8, 141.5, 131.9, 131.3, 129.2, 128.4, 126.4, 123.8.

Anal. Calcd. for $C_{28}H_{14}N_2O_4S_2$: C, 66.39; H, 2.79; N, 5.53; Found: C, 65.25; H, 2.72; N, 5.58.

Method B: *N*-Phenyl-4,5-dichlorophthalimide (**2**, 10.69 g, 36.61 mmol) and anhydrous sodium sulfide (2.88 g, 36.9 mmol) were reacted in DMAc at 160 °C for 12 h under nitrogen. Upon cooling to ambient temperature, the yellow product precipitated, and was filtered, washed with water and CH_3OH, and vacuum dried at 65 °C; yd 8.06 g (87%); spectral analysis confirmed that the product was the same as with method A.

Thianthrene-2,3,7,8-tetracarboxylic acid (6). *N,N*-Diphenylthianthrene-2,3,7,8-tetracarboxylic bisimide (**5**, 11.23 g, 22.17 mmol) was refluxed in a solution of sodium hydroxide (10.70 g, 268 mmol) in 150 mL of water for 16.5 h. After cooling to ambient temperature, the reaction solution was filtered to remove insoluble material. The filtrate was acidified with dilute HCl to give a white precipitate. The product was collected by filtration, washed with water and dried under vacuum; yd 8.63 g (99%); mp > 360 °C (dec); FTIR (KBr): 3436, 3271, 3092, 3028, 2605, 1721, 1677,1538, 1287,1225, 1152, 1104 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.85; ^{13}C NMR (DMSO-d_6): 167.4, 136.4, 132.9, 128.5.

Thianthrene-2,3,7,8-tetracarboxylic dianhydride (7). Thianthrene-2,3,7,8-tetracarboxylic acid (**6**, 1.82 g, 4.64 mmol) was stirred in 35 mL of acetic anhydride at 100 °C for 8 h under nitrogen. The mixture remained heterogenous, but turned yellow during the reaction. Acetic acid was removed by vacuum distillation. The yellow solid was filtered, rinsed with acetic anhydride, washed with hot benzene and dried under vacuum; yd 1.16 g (70%); mp 349-350 °C; FTIR (KBr pellet): 1846, 1802, 1782, 1308, 1254, 1245, 898, 732cm^{-1}; ^{13}C NMR (DMSO-d_6): δ 161.8, 141.7, 131.6, 125.1.

Thianthrene Containing Poly(amic acid)s (8).[12] A typical polymerization procedure was as follows. To a solution of 4,4'-oxydianiline (0.4000 g, 1.998 mmol) in 10 mL of DMAc was added thianthrene-2,3,7,8-tetracarboxylic dianhydride (**7**, 0.7119 g, 1.998 mmol) in several portions. The mixture was stirred at ambient temperature for 16 h under nitrogen. The viscous polymerization solution was diluted with 30 mL of DMAc and precipitated into 400 mL of CH_3OH. The polymer was collected by filtration, washed with hot CH_3OH and dried under vacuum; yd 1.113 g (100%); FTIR (solvent-cast film): 3281, 3060, 2608, 1716, 1655,1606, 1502, 1247, 1220 cm^{-1}; ^{13}C NMR (DMSO-d_6): δ 166.3, 165.4, 152.8, 138.4, 137.4, 137.2 (shoulder), 134.8, 134.4, 130.4, 129.3, 127.9, 121.3, 118.7.

Results and Discussion

Monomer Synthesis

Several sulfur nucleophiles were used to determine the reactivity of *N*-phenyl-4,5-dichlorophthalimide (**2**) to substitution and compare it to the mono-substituted derivative, *N*-phenyl-4-chlorophthalimide (**9**). Both compounds have an imide carbonyl

para to the chlorine substituents which activate for NAS via polarization and resonance stabilization (Figure 1). It has been shown that **9** reacts in high yields with thiophenoxide and Na_2S to give *N*-phenyl-4-thiophenoxyphthalimide and 4,4'-thiobis(*N*-phenyl)phthalimide, respectively.[14,15] Both chlorine positions of **2** reacted with thiophenoxide at 100 °C to give *N*-phenyl-4,5-dithiophenoxyphthalimide (**3**). Figure 2 shows the ^{13}C NMR spectra of **2** and **3**. When half the amount of thiophenoxide and lower temperature were used, only one chlorine was substituted to give *N*-phenyl-4-thiophenoxy-5-chlorophthalimide (**4**) as the major product (> 90%) (Figure 3). This result is contrary to earlier reports of enhanced NAS of chlorinated aromatics with thioether substituents which were claimed to cause an electron withdrawing inductive effect which activated the aromatic ring (more than chlorine) for NAS.[16,17] This effect was correlated with ^{13}C NMR chemical shifts; ie, carbons ortho to the thioether substituent showed greater downfield shifts.[18] Apparently for **4**, the first thiophenoxy group sterically blocks substitution of the adjacent chlorine and higher temperatures are needed to complete the reaction. *N*-Phenyl-4,5-dichlorophthalimide (**2**) was more reactive than *N*-phenyl-4-chlorophthalimide (**9**), indicating that the o-chlorine substituent activates more than it sterically hinders NAS. This was determined by dissolving equal amounts of **2** and **9** in DMAc and slowly adding one-half equivalent of thiophenoxide (Figure 4). The ^{13}C NMR spectrum of the isolated product indicated that **2** was completely consumed to give **4**, leaving unreacted **9**.

The above results confirmed reactivity of both chlorine substituents of **2**, although there was an obvious decrease in reactivity after substitution of the first

chlorine. Additional reactions were done to determine if 4,4'-thiobis(*N*-phenyl-5-chlorophthalimide) (**10**) could be selectively synthesized. This would allow eventual synthesis of 4,4'-thiobis(5-chlorophthalic anhydride) (**11**) (Figure 5) which could be used to make chlorinated polyimides. Earlier work showed that polymers derived from dianhydrides and dicarboxylic acids with chlorine substituents ortho to the aryl linkage group were considerably more soluble than analogous unsubstituted polymers.[18,19] However, when **2** was reacted with only half an equivalent of Na_2S, *N,N'*-diphenylthianthrene-2,3,7,8-tetracarboxylic bisimide (**5**) and starting material (**2**) were the major compounds isolated. This indicates that 4,4'-thiobis(5-chlorophthalimide) (**10**) is more reactive than **2** under these conditions. In other words, the o-thiophenoxy substituent apparently activates for NAS here more than the o-chlorine substituent. The smaller Na_2S nucleophile is less sterically hindered than thiophenoxide, and substitution of the second chlorine of **2** was faster than the first, in contrast to reaction with thiophenoxide where the second substitution step was slower and required higher temperatures to obtain the disubstituted product, **3**.

Thiobenzamide has also been shown to form thioether bonds and was used here in an effort to enhance formation of **10**. This attempt failed and instead gave quantitative yields of **5** (based on sulfur equivalents) and recovered starting material (**2**). Although the mechanism for which thiobenzamide forms the thioether bonds was not determined, this result indicates factors similar to those for Na_2S control reaction from thiobenzamide and base.

Figure 6 shows the overall synthetic route used for thianthrene-2,3,7,8-tetracarboxylic dianhydride (**7**). *N*-Phenyl-4,5-dichlorophthalimide (**2**) was prepared in good yield from 4,5-dichlorophthalic anhydride (**1**) and aniline. Bisimide **5** was then prepared by two methods. Method A was developed first while exploring new possibilities for synthesizing polymers with both imide and thiazole functionalities on the same aromatic ring.[11] The proposed reaction involved sequential NAS of the two chlorine sustituents of **2** by first the sulfur and then the nitrogen of thiobenzamide to form a fused thiazole ring. However, substitution only occurred with sulfur, and the intermediate thiobenzamide lost benzonitrile which results in intermolecular NAS leading to *N,N*-diphenylthianthrene-2,3,7,8-tetracarboxylic bisimide (**5**) in 90% yield. Figure 7 shows the ^{13}C NMR spectra of **2** and **5**. Thioacetamide was briefly used as the sulfur source (lower cost), but it is a cancer suspect agent, and its use was discontinued. When these reactions were carried out in the absence of solvent, they gave low yields with many side-products.

Method B was then developed because it reduced overall cost and gave yields of > 85%. This approach can be further modified by using the *N*-methyl-substituted phthalimide which offers further advantages of low cost and ease of purification.[12] Hydrolysis of bisimide **5** followed by acidification gave tetracarboxylic acid **6**. Dianhydride **7** was formed by dehydrating **6** in acetic anhydride at 100 °C. Higher temperatures (ie., reflux) caused side reactions which gave lower yields. Figure 8 shows the ^{13}C NMR spectra of **6** and **7**.

Polymer Synthesis

Thianthrene-base polyimides were prepared by the conventional two-step process. The first step consisted of reacting dianhydride **7** with aromatic diamines in DMAc at low temperatures to give poly(amic acid)s (**8**). The second step involved thermal cyclization of solution-cast films to give the respective polyimides. Figure 9 shows schematically the polymerization of thianthrene-2,3,7,8-tetracarboxylic dianhydride (**7**) with aromatic diamines; yields were quantitative in all cases and the poly(amic acid) intermediates had intrinsic viscosities in the range of 0.15-0.5 in DMAc at 30 °C (Table 1).

The free-standing films were made by casting DMAc solutions of the poly(amic acid)s onto a dust-free glass plate and vacuum drying at ambient temperature until tack-free. The films were cured under a dynamic nitrogen atmosphere at 30 °C for 0.5 h and at 100, 200 and 300 °C each for 1 h. After cooling to ambient temperature, the amber colored films were removed by soaking in warm water. Figure 10 shows a typical set of FTIR spectra for the cyclization process obtained using a heated IR cell. Disappearance of the peaks at ca 1220 and 1544 cm^{-1} were diagnostic for reaction of the amide and acid residues. Appearance of new peaks at ca 1365 and 1775 cm^{-1} confirmed imide formation.

Films obtained from thianthrene dianhydride and ODA or MDA were creasible as opposed to those derived from 1,3- and 1,4-phenylenediamine which were brittle. Table 1 includes the thermal analysis data for the prepared polyimides. Degradation onset was above 425 °C in both N_2 and air atmospheres and char yields were > 60 %

for all the polymers in N_2 atmosphere at 800 °C. Figure 11 gives the TGA traces of the oxydianiline polyimide in air and N_2; even in air, significant weight loss is not seen below 500 °C. Although the thianthrene containing polyimides have low crystallinity (as determined by wide angle X-ray analysis performed on the films), the polymers were soluble only in sulfuric acid.

Conclusions

Nucleophilic aromatic substitution of *N*-phenyl-4,5-dichlorophthalimide with sulfur nucleophiles was accomplished with relative ease and in high yields. The dichloro-substituted phthalimide was more reactive than the mono-substituted derivative, and after being substituted once, the reactivity of the second chlorine was increased for Na_2S attack but reduced due to steric hindrance for C_6H_5SNa attack.

Thianthrene-2,3,7,8-tetracarboxylic dianhydride was prepared starting from dichlorophthalic acid, making the *N*-phenylimide, forming the thianthrene ring with either thioamides or sodium sulfide, hydrolyzing the imide rings and dehydrating the acids to the anhydrides. Polyimides were synthesized by the low temperature formation of poly(amic acid) solutions which were cast into films and then thermally cyclized. Polyimides derived from flexible diamines gave creasible films while rigid diamines gave brittle films. Although polymer solubility was not enhanced by incorporating the bent thianthrene structure as was hoped initially, the polyimides displayed excellent thermal stability.

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List of Figures

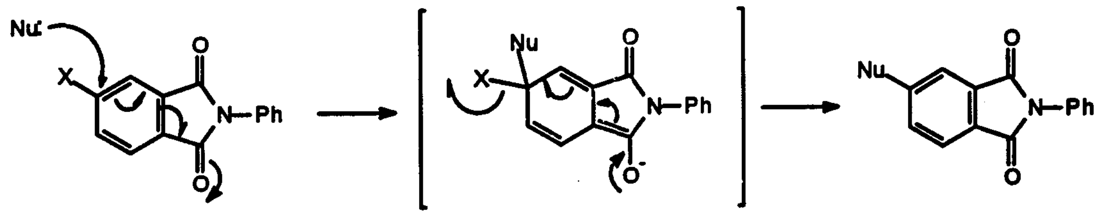


FIGURE 1

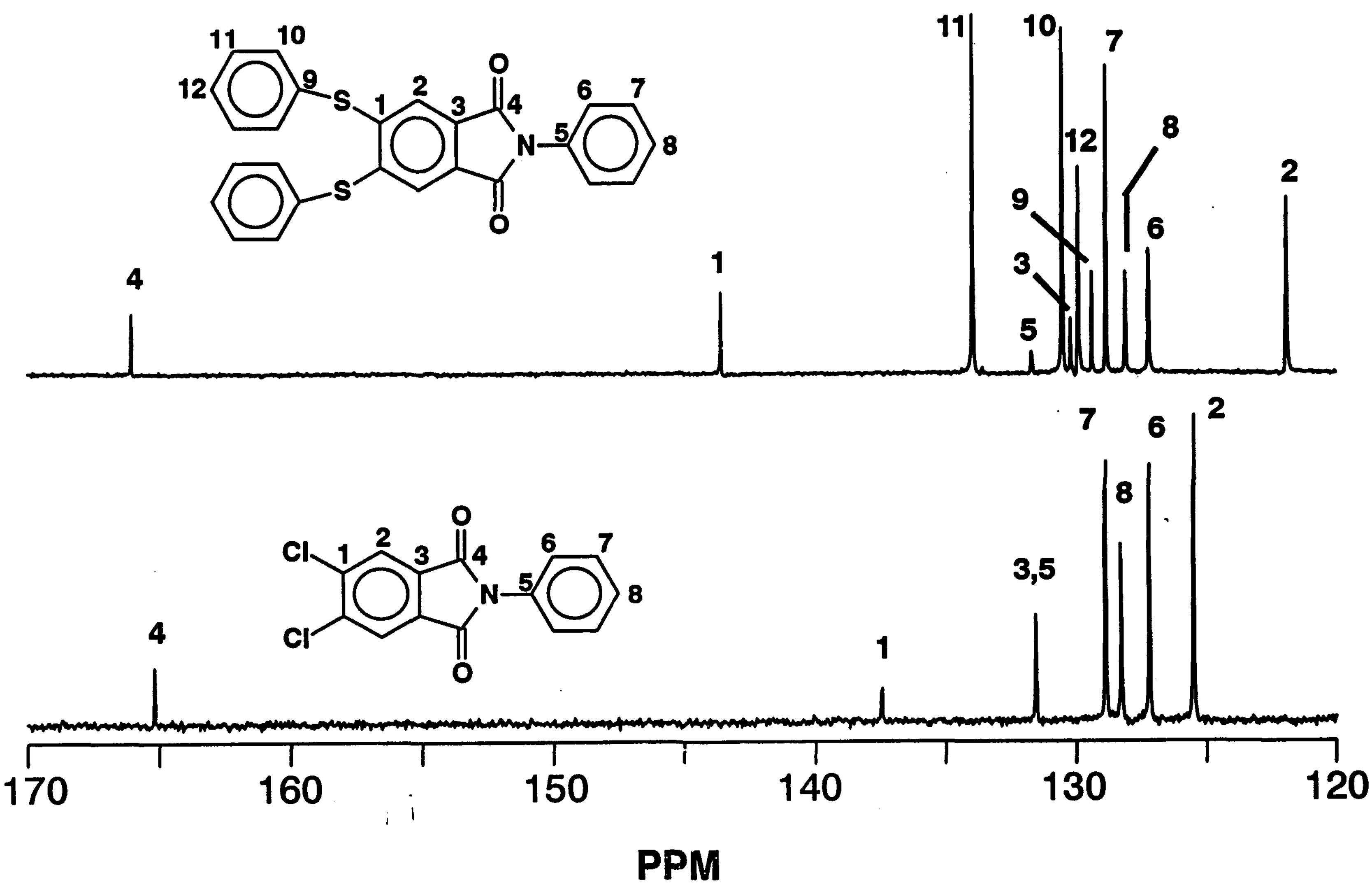


Figure 2

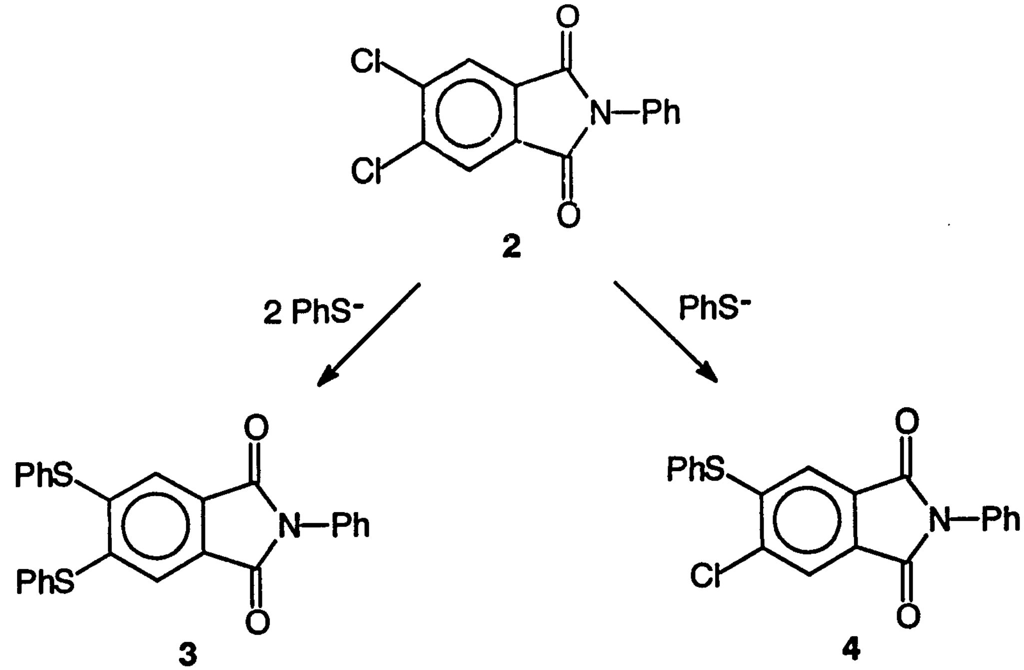
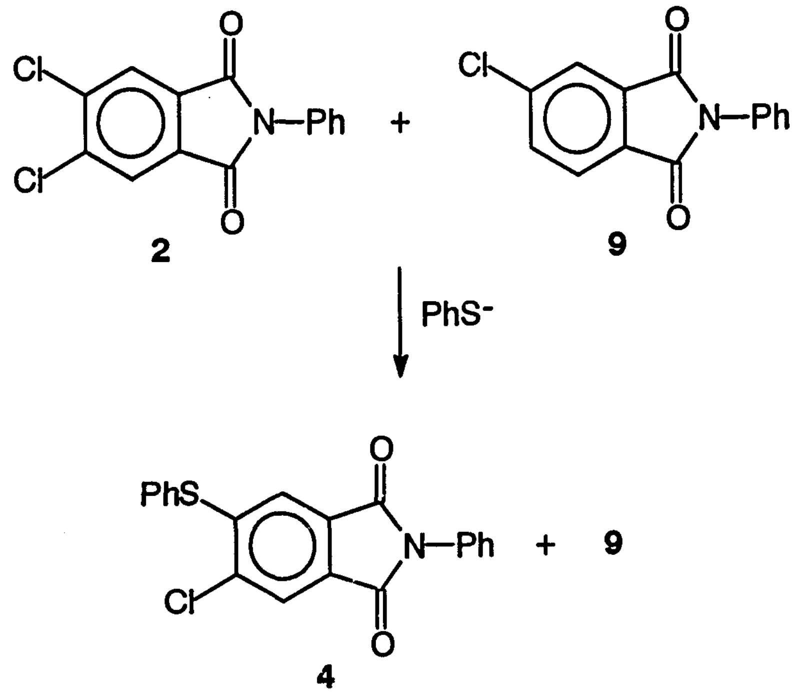


FIGURE 3



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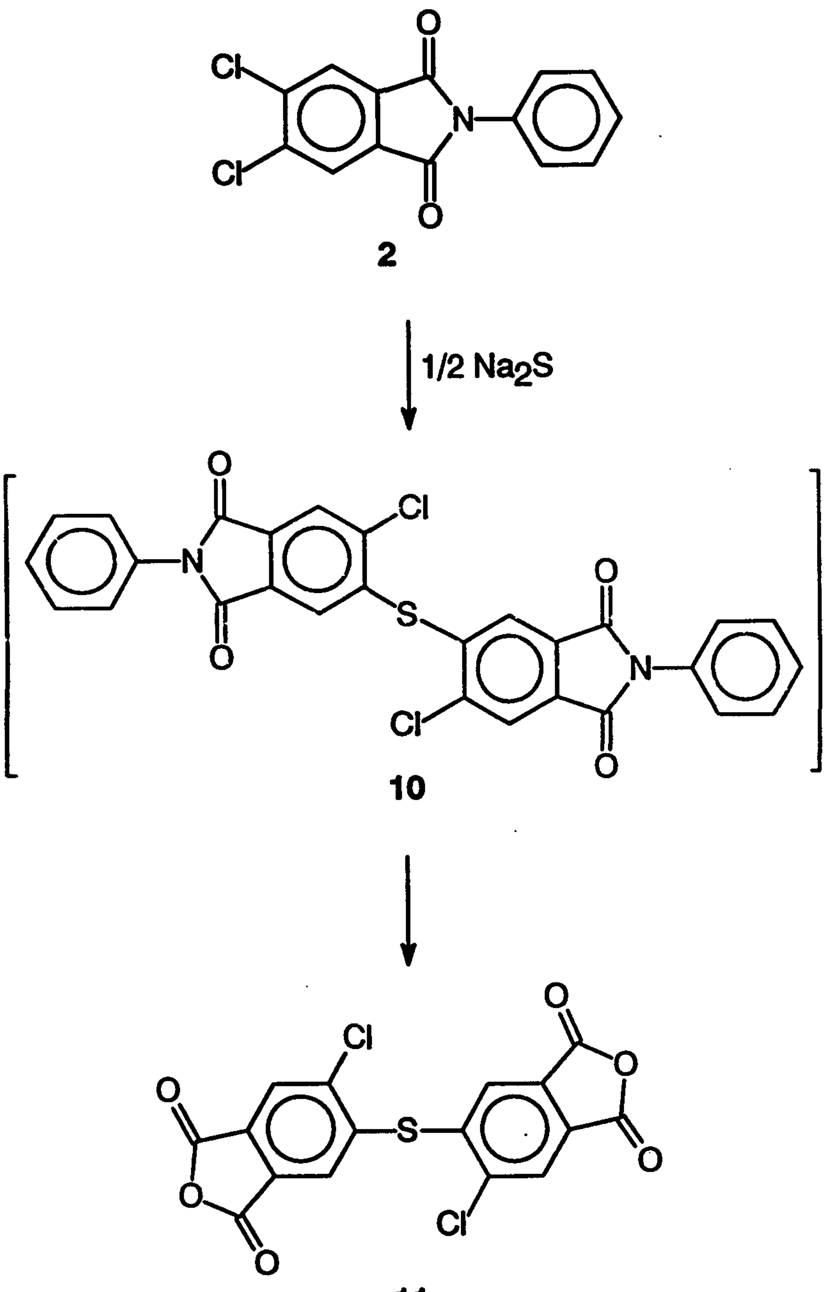

Figure 5

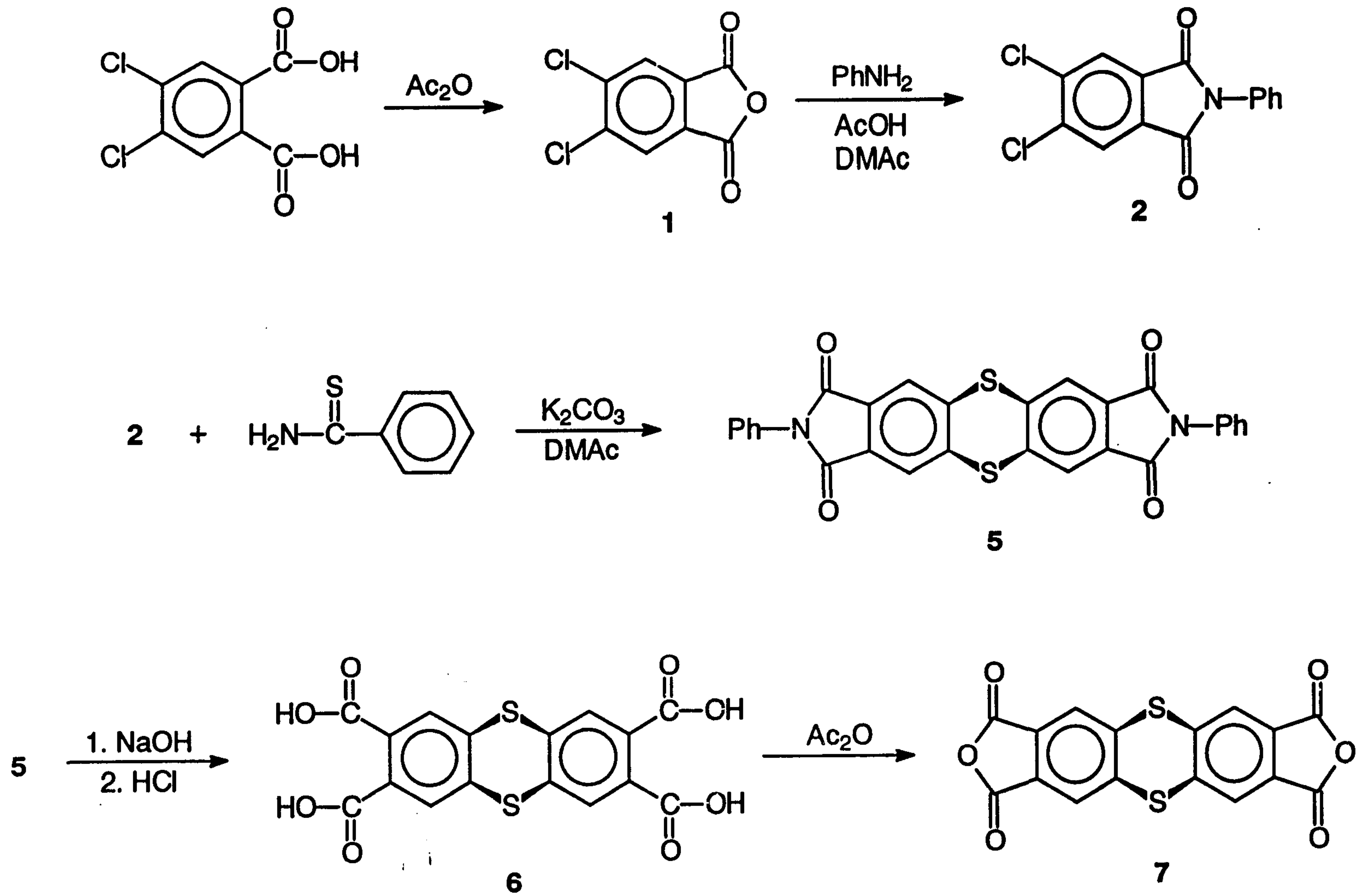

Figure 6

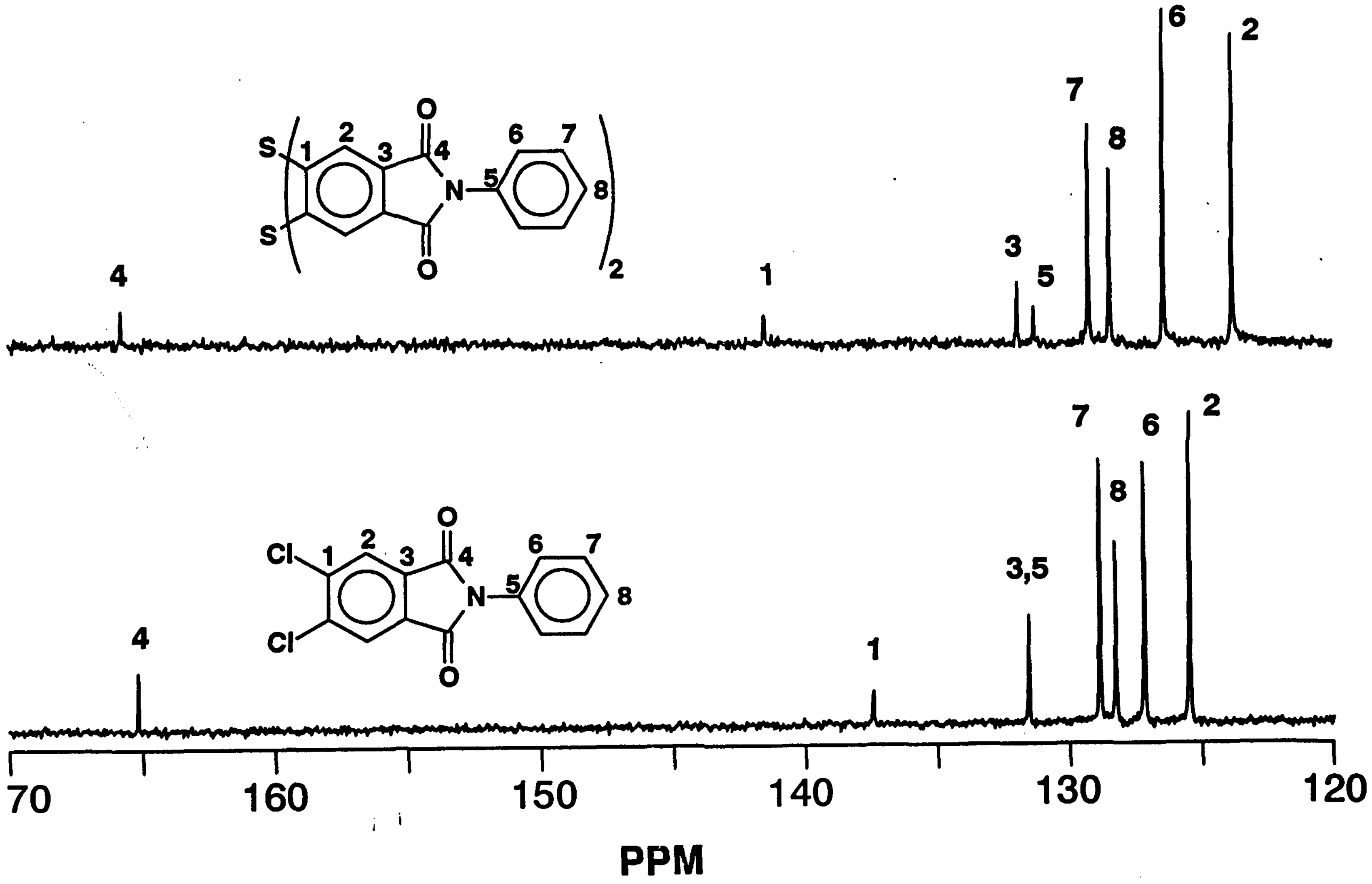

Figure 7

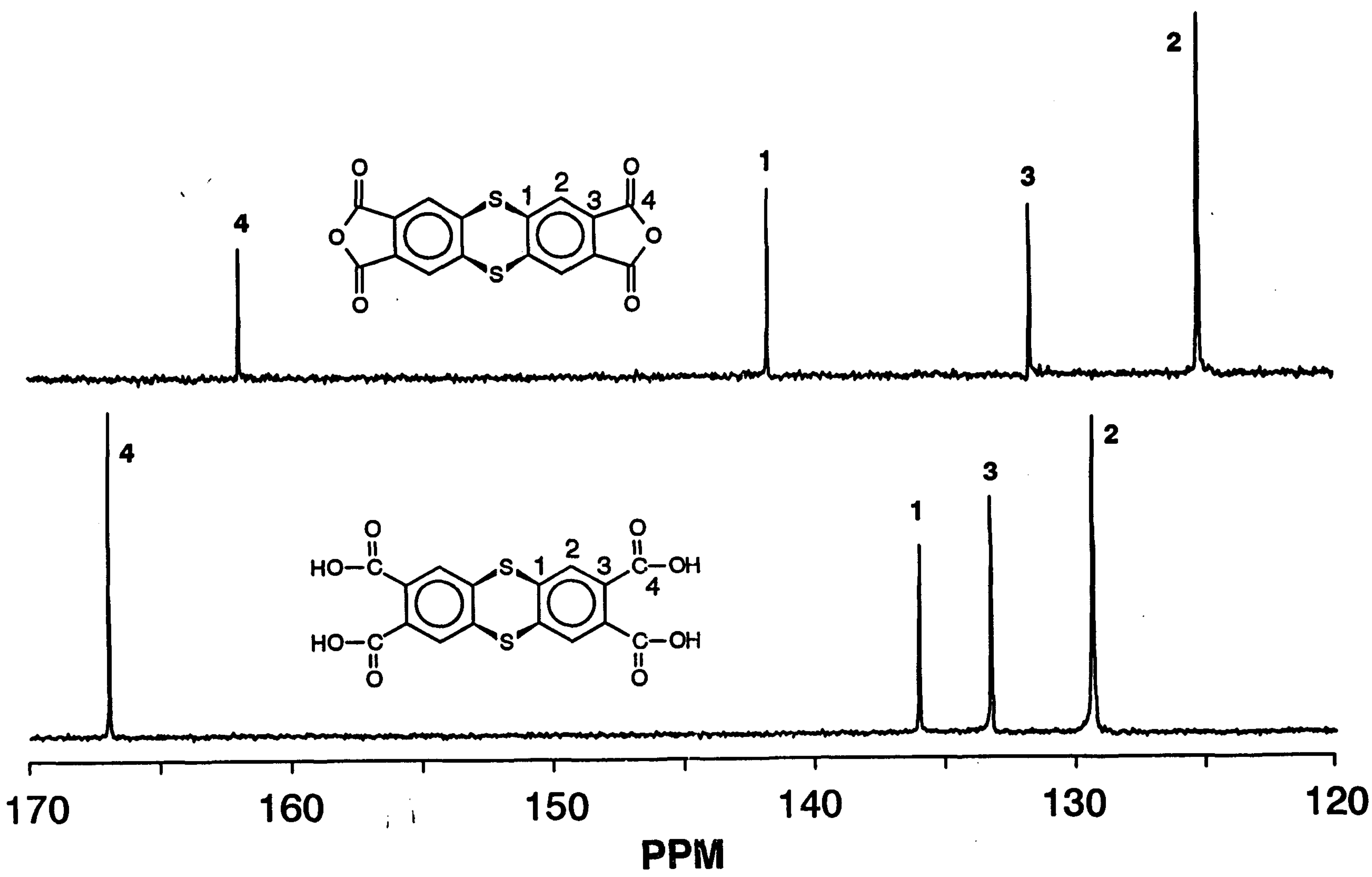

Figure 8

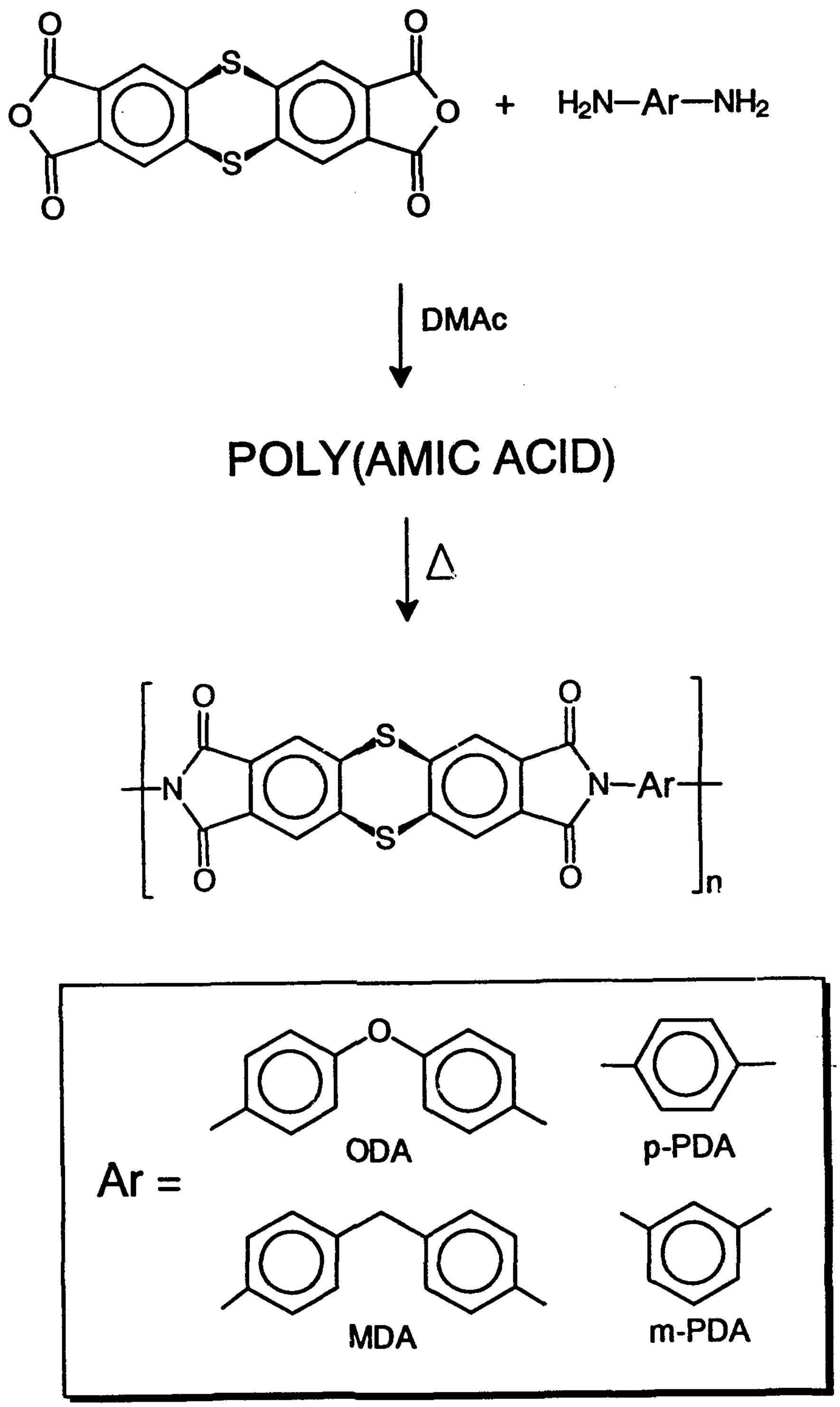

Figure 9

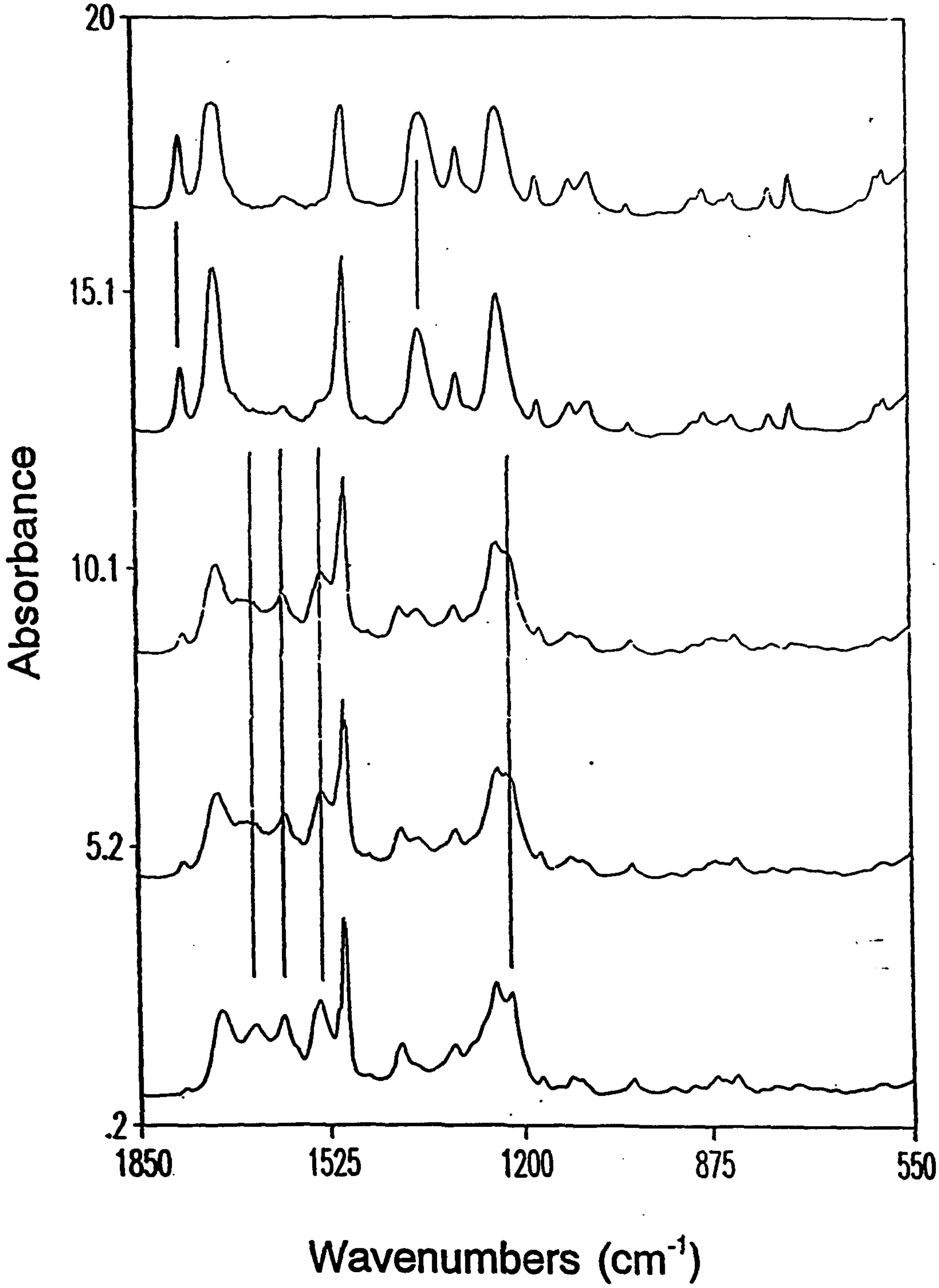
20
15.1
10.1
5.2
.2
Absorbance
1850
1525
1200
875
550
Wavenumbers (cm^{-1})

Figure 1D

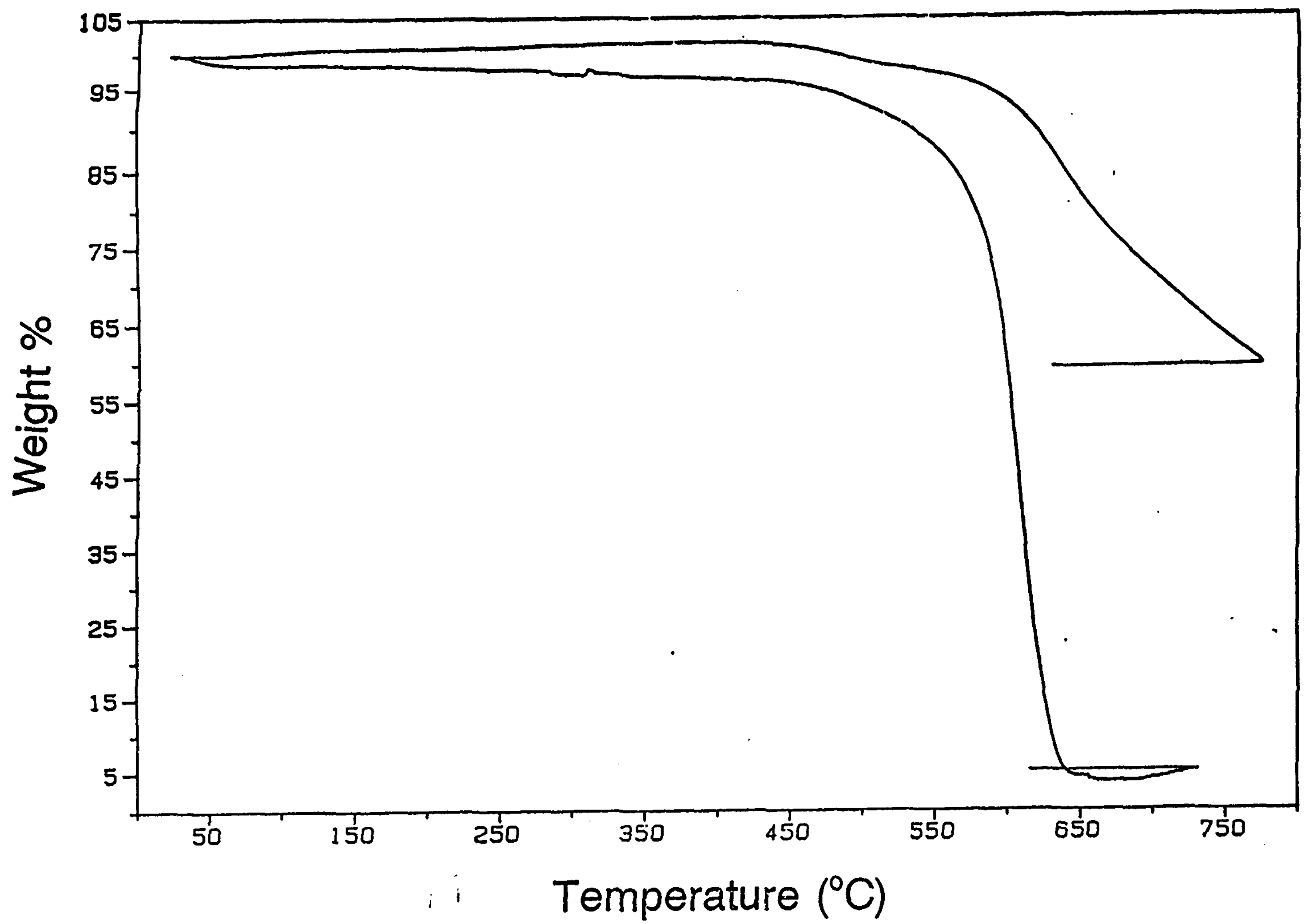
Weight %
105
95
85
75
65
55
45
35
25
15
5
50
150
250
350
450
550
650
750
Temperature (°C)

Table 1 Polyimide properties.

POLYIMIDE	$[n]$ dL / g	TGA[b] loss temperature (°C)			
		onset temp. (N_2 / air atm.)		10% wt. loss (N_2 / air atm.)	
7 - ODA	0.82	428	428	562	566
7 - MDA	0.25	435	427	573	563
7 - pPDA	0.46	434	414	564	543
7 - mPDA	0.18	414	421	576	561

[a] Intermediate poly(amic acid)s measured in DMAc at 30 °C.

[b] Measured at heating rate of 10 °C/min.